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<b>(54) Title:</b> SELF-FOAMING MULTIFUNCTIONAL CLEANSING COMPOSITION  <b>(57) Abstract</b>  A stable post-foaming cleansing composition including a surfactant; a compatible suspending agent; a low to nonpolar liquid that serves as an auxiliary (suspensate); a lather-generating agent to provide self-lathering; and water.		

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## SELF-FOAMING MULTIFUNCTIONAL CLEANSING COMPOSITION

This invention relates to a novel stable, aqueous self-foaming cleansing composition. More particularly, this invention relates to a stable self-foaming cleansing composition incorporating a self-foaming agent, an active suspensate and low levels of a surface active agent.

There are many cleansing products for personal and home use for example shampoos, skin cleansers, soaps and hard surface cleaners. The products can take the form of a liquid, a gel or paste of various viscosities. These products have various amounts of various essential and optional ingredients or components selected for their intended function or use. One of the principal components in most cleansing products is a surfactant. Surfactants are used to remove dirt and debris and also to impart a foaming characteristic to the cleansing product which gives the consumer a perceived indication that the product is functioning as a cleanser. In addition to a surfactant, some cleansing products may contain an active ingredient, to impart a secondary function to the product. However, these additional ingredients tend to suppress the foaming action of surfactants.

In recent years, there have been attempts to incorporate higher levels of active ingredients into a surfactant-based product formulation to give the consumer the benefit of having one product with dual functions. For example, a shampoo with conditioner. These dual function products are sometimes referred to as "two-in-one" or "2-in-1" products because there is an active component and a surfactant, or blend of surfactants, in one formulation. In these systems, the surfactant is combined with a auxiliary active ingredient such as a conditioning agent. The object of 2-in-1 products is to optimize the deposition of the auxiliary active component onto the surface to be cleaned while maintaining both the maximum cleaning and lathering properties of the formulation.

As aforementioned, the problem with trying to combine an active component into a surfactant-based formulation has to do with competing functions of ingredients, that is, the use of one or more actives in a formulation may suppress the foaming characteristic of the surfactant. Thus, when a hydrophobic auxiliary active, such as a hydrophobe, is used in a formulation, normally the amount of surfactant in the formulation is increased so that the formulation will provide a level of foaming and cleansing which is acceptable to the consumer. However, in prior art formulations, as the amount of surfactant used in the formulation is increased, the lower the amount of active which is deposited onto a surface. Thus, at high levels of surfactant, the beneficial effect of the active is lost. Conversely, if the level of surfactant is maintained then the level of the active component must be lowered and the beneficial effects of the auxiliary active is lost.

Even so, current 2-in-1 products simply cannot contain low levels of surfactant because without employing a certain high level of surfactant, the 2-in-1 products known in the

prior art would not produce consumer-acceptable lather. Therefore, there must be a compromise between the amount of surfactant used and the amount of actives used in a surfactant-based formulation in order to obtain the maximum beneficial effect from both the foam-producing surfactant and the active used.

5 In addition, high levels of the most efficient cleansing surfactants may produce either a skin irritation or damage to the surface to which it is applied. Thus there is a practical limit to the amount of surfactant one can use in products which will contact the skin of consumers or the surface to be cleaned in order to minimize the detrimental effect.

In order to provide the best possible cleansing composition, it would be desirable  
10 to maximize the amount of auxiliary active ingredient in a surfactant-based formulation which translates to maximum deposition of the active ingredient on a surface to be cleaned while maintaining the required amount of surfactant necessary to obtain an acceptable foaming and cleansing product for a consumer.

It has been unexpectedly found that by adding a self-foaming agent to a  
15 surfactant-based formulation having at least one active ingredient, the surfactant levels required to obtain a consumer-acceptable foam is reduced providing a mechanism for increasing the amount of active ingredient in the formulation without detrimentally affecting the foaming characteristics of the formulation.

In accordance with the present invention, there is provided a self-foaming  
20 cleansing composition including a surfactant; a compatible suspending agent; a suspensate adapted to be deposited onto a surface to be cleaned; a lather-generating agent to provide self-lathering; and water.

The present composition enables the use of low surfactant levels thereby lowering irritation yet maximizing the deposition of the suspensate and its contents to  
25 maximize functionality. While the present invention is not limited to any specific theory of action, it should be of interest and may be helpful in understanding the present invention, if the following explanation is offered for the surprising discovery that reduced levels of surfactant are possible for surfactant-based formulation and still maintaining acceptable levels of foam and cleansing.

30 In a conventional surfactant-based cleansing system, the foam is generated by the entrapment of air from the surrounding atmosphere. This is accomplished by creating sites of nucleation for the air in the surfactant-based liquid. Typically, the mechanical action of rubbing the hands together, or rubbing the hands on the hair, or rubbing a sponge or brush on a surface will provide suitable sites of nucleation and consequently will generate a foam. The  
35 quality and quantity of the foam produced is dependent on the nature and dilution of the surfactant, the type and amount of mechanical action and the presence of dirt, oil or other matter on the surface that can modify the foam.

The addition of a auxiliary active, such as a hydrophobic oil, will usually reduce the ability of the system to generate a foam. Consequently, more surfactant is needed to achieve the same level of perceived cleaning.

However, if a foam-generating agent is added to the surfactant base little or no mechanical action is needed to produce an acceptable foam. The release of the entrapped foaming agent results in self-nucleation of a bubble in the surfactant solution. Further, the lather forming abilities of a system with a self-foaming agent is so efficient that the level of surfactant can be greatly reduced without affecting the quality or quantity of foam produced.

Analogously, if a auxiliary active component is added, the presence of the self-foaming agent can overcome the foam suppressing effect of the auxiliary active component on the primary surfactant or blend of surfactants. As a result higher levels of auxiliary active can be incorporated into the cleansing system without reducing the quality or quantity of lather produced. In fact, the level of primary surfactant can be greatly reduced without adversely affecting foaming resulting in a greater deposition of the auxiliary active component or components.

It is one of the objectives of the present invention to provide a novel surfactant-based multifunctional formulation, for example, a 2-in-1 formulation, containing a self-foaming agent useful for a wide range of cleansing products. The composition of the present invention delivers more functional materials than conventional 2-in-1 products due to the lower surfactant levels. The lower surfactant levels are also less harsh to skin and hair and other surfaces.

Figure 1 is a graphical illustration of the amount of deposition of peanut oil on a surface using certain formulations of the present invention.

Figure 2 is a graphical illustration of the amount of deposition of peanut oil on a surface using certain formulations of the present invention.

Figure 3 is a graphical illustration of the amount of deposition of silicone oil on a surface using certain formulations of the present invention.

Figure 4 is a graphical illustration of the cleaning efficacy of certain formulations of the present invention.

Figure 5 is a graphical illustration of the foaming height of certain comparative formulations.

Figure 6 is a graphical illustration of the foaming height of certain formulations of the present invention.

In its broadest scope, the present invention is a stable, homogeneous, self-foaming composition which includes, as essential components, water; an effective amount of a suitable surfactant adapted to provide the required cleansing and foaming properties to the composition; an effective amount of a selective suspending agent adapted to suspend an active suspensate which is to be deposited on a surface to be cleaned; an effective amount of a

selective suspensate adapted to function as its intended use, and an effective amount of a selective self-foaming agent adapted to provide the resultant composition with self-lathering properties.

By "stable" it is meant that the composition of the present invention remains suitably homogeneous, that is, free from separation, flocculation, creaming or syneresis, to deliver the desired performance properties for at least a two year period of time under normal use conditions.

By "self-foaming" or "self-lathering" it is meant that little to no mechanical action is needed to produce a consumer acceptable level of foam.

By "homogeneous" it is meant uniform in structure or composition throughout.

Water is an essential component of the composition of the present invention because it serves as a diluent and a solvent for the entire matrix, and allows the suspending agent to stabilize the suspensate(s) of the composition. Water from any source, including, for example, tap water, distilled water, deionized water is suitable for use in the present invention. The amount of water in the total composition ultimately is determined by the amount of the other essential and optional ingredients included in the composition. Preferably demineralized water is used. Generally, the water used is from 1.0 percent to 99 percent by weight. Preferably, from 35 percent to 95 percent by weight of the composition should be water and, more preferably, from 60 percent to 90 percent by weight of the total composition should be water.

The composition of the present invention includes as an essential constituent at least one or more surface active agents (surfactants). These materials reduce the surface tension of water and create a suitable interfacial tension between the water and particulate matter, oil and gases having a positive absolute vapor pressure at use conditions so as to generate foam and remove dirt and debris from the surface. The surfactant used in the composition of the present invention can be for example an anionic, nonionic, amphoteric (zwitterionic), cationic or mixtures thereof.

Suitable anionic surfactants include alkyl and alkyl ether sulfates, or combinations thereof. These surfactants have the respective formula  $\text{ROSO}_3\text{M}$  and  $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$  wherein R is an alkyl or alkenyl radical or preferably 8 to 22 and, more preferably 10 to 18 carbon atoms, x is 0 to 10 and M is a water-soluble cation such as ammonium, sodium, potassium, and triethanolamine.

Other suitable anionic surfactants include acyl sarcosines derived from natural fatty acids and amino acid sarcosine (N-methyl glycine) of the following formula



where R is a fatty acid hydrocarbon chain from 10 to 20 carbon atoms, and M is a water-soluble cation such as ammonium sodium, potassium triethanolamine, etc. Common derivatives include lauroyl, myristoyl, oleoyl, and stearoyl sarcosinates.

Other suitable anionic surfactants include alkyl and alkylbenzene sulfonate, succinates, sulfoacetates, and sulfosuccinates having from 8 to 24 carbon atoms. Suitable derivatives include the ammonium, sodium, potassium, and triethanolamine salts thereof.

Nonionic synthetic detergents can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which can be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. Another class has semi-polar characteristics. Classes of nonionic synthetic detergents are as follows:

(1) The monoethanol, diethanol, and ammonia amides of fatty acids having an acyl moiety of from 8 to 18 carbon atoms. These acyl moieties are normally derived from naturally occurring glycerides, for example, coconut oil, palm oil, soybean oil and tallow, but can be derived synthetically, for example, by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process.

(2) A class of nonionic synthetic detergents under the trade name of Pluronic®. These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water insolubility, has a molecular weight of from 1500 to 1800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole and the liquid character of the product is retained up to the point where the polyethylene content is about 50 percent of the total weight of the condensation product.

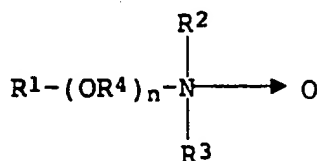
(3) The polyethylene oxide condensates of alkyl phenols, for example, the condensation products of alkyl phenols, having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octene, or nonene, for example.

(4) Those nonionic synthetic detergents derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. For example, compounds containing from 40 to 80 percent polyoxyethylene by weight and having a molecular weight of from 5,000 to 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide.



(5) The condensation product of aliphatic alcohols having from 8 to 22 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, for example, a coconut alcohol ethylene oxide condensate having from 5 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

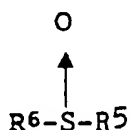
(6) Long chain tertiary amine oxides corresponding to the following general formula



wherein R<sup>1</sup> is an alkyl radical of from about 8 to about 24 carbon atoms, R<sup>2</sup> and R<sup>3</sup> are each methyl, ethyl or hydroxyethyl radical, R<sup>4</sup> is ethylene, and n equal from 0 to about 10. The arrow in the formula is a conventional representation of a semi-polar bond. Specific examples of amine oxide detergents include dimethyldodecylamine oxide; cetyldimethylamine oxide; bis-(2-hydroxyethyl) dodecylamine oxide; and bis-(2-hydroxyethyl)-3-dodecoxy-1-hydroxypropyl amine oxide.

(7) Long chain tertiary phosphine oxides, corresponding to the following general formula RR'R"P→O wherein R is an alkyl, alkenyl or monohydroxyalkyl radical ranging from 10 to 24 carbon atoms in chain length and R' and R" are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond. Examples of suitable phosphine oxides are found in U.S. Pat. No. 3,304,262 of Feb. 14, 1967 and include: dimethyldodecylphosphine oxide; diethyldodecylphosphine oxide; dimethyl-(2-hydroxydodecyl) phosphine oxide.

(8) Long chain sulfoxides having the formula



wherein R<sup>5</sup> is an alkyl radical containing from 10 to 28 carbon atoms, from 0 to 5 ether linkages and from 0 to about 2 hydroxyl substituents, at least one moiety of R<sup>5</sup> being an alkyl radical containing 0 ether linkages and containing from 10 to 18 carbon atoms, and wherein R<sup>6</sup> is an alkyl radical containing from 1 to 3 carbon atoms and from one to two hydroxyl groups. Specific examples of these sulfoxides are: dodecyl methyl sulfoxide; 3-hydroxy tridecyl methyl sulfoxide; 3-methoxy tridecyl methyl sulfoxide; and 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

Amphoteric synthetic detergents can be broadly described as derivatives of aliphatic secondary and tertiary amines, in which the aliphatic radical may be straight chain or

branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing groups, for example, carboxy, sulfo, sulfato, phosphato, or phosphono. Examples of compounds falling within this definition are sodium-3-dodecylamino-propionate and sodium-3-dodecylaminopropane sulfonate.

5                Zwitterionic synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radical may be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group, for example, carboxy, sulfo, sulfato, phosphato, or phosphono. Examples of  
10 compounds falling within this definition are 3-(N,N-dimethyl-N-hexadecylammonio) propane-1-sulfonate and 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxy propane-1-sulfonate.

Cationic detergents include those having the formula  $R-N(R^2)_3(+)X(-)$  wherein R is an alkyl chain containing from 8 to 20 carbon atoms, each  $R^2$  is selected from the group consisting of alkyl and alkanol groups containing from 1 to 4 carbon atoms and benzyl groups  
15 there being normally no more than one benzyl group and two  $R^2$  groups can be joined by either a carbon-carbon ether, or imino linkage to form a ring structure, and X represents a halogen atom, sulfate group, nitrate group or other pseudohalogen group. Specific examples are coconut alkyl trimethyl amine chloride, dodecyl dimethyl benzyl bromide, and dodecyl methyl morpholino chloride.

20                The surfactant is present in the composition of the present invention in an effective amount to reduce the surface tension of water and to create a suitable interfacial tension so as to cleanse the surface of materials not normally removed by water alone and to generate a suitable foam. The amount of surfactant used in the composition of the present invention should be sufficient to provide the desired cleansing and foaming. Below the  
25 preferred amounts discussed herein below, the composition will not provide adequate cleaning and foaming. Above the preferred amounts, the amount of surfactant will be too high and the deposition of the active ingredient will not be sufficient. Furthermore, too high levels of surfactant will irritate the skin of a consumer or degrade the surface the composition is applied to. In addition, use of any of the ingredients in the present invention above the  
30 preferred amounts would not be economical.

Generally, the surfactant is present in the composition in an amount of from 0.001 percent to 50 percent by weight of the composition. Preferably, the surfactant is present in an amount of from 0.01 percent to 10 percent by weight based on the weight of the composition. More preferably, the surfactant is present in an amount of from 0.1 percent to 5  
35 percent by weight based on the total weight of the composition. It has been found that even at the above low levels the formulation generates sufficient foam acceptable to the consumer.

A nonionic, anionic, cationic or amphoteric surfactant, may be used alone, in the composition of the present invention; or one or more surfactant may be used as a mixture, the

surfactants selected from anionic, nonionic, cationic, and amphoteric surfactants to provide the composition of the invention. Numerous surface active agents or surfactants, suitable for use in the present composition, are described in detail in McCutcheon's "Emulsifiers and Detergents", 1991 and in U.S. Patent Nos. 3,723,357; 3,964,500; 4,788,006; 4,364,837; 5 4,491,539, and 4,678,606. Preferred examples of anionic surfactants useful in the present invention include ammonium lauryl sulfate, ammonium cocoyl isethionate, sodium laureth-2 sulfate, TEA-lauryl sulfate, ammonium laureth 2 sulfate, sodium laureth-13 carboxylate, sodium lauryl sarcosinate, sodium methyl cocoyl taurate, sodium lauroyl lactylate, sodium dodecyl benzene sulfonate, potassium coco-hydrolyzed animal protein sodium C12-14 olefin sulfonate, 10 sodium cocoyl glutamate, and disodium cocamido MEA-sulfosuccinate. Preferred examples of nonionic surfactants useful in the present invention include lauramide DEA, cocamide MEA, PEG-7 glyceryl cocoate, and dimethicone copolyol. Preferred examples of cationic surfactants useful in the present invention include isostearyl ethyldimonium ethosulfate, PEG-10 stearamine, and cocoyl benzyl hydroxyethyl imidazolinium chloride. Preferred examples of 15 amphoteric surfactants useful in the present invention include lauroamphodiacetate and sodium C12-15 alkoxypropyl iminodipropionate.

The composition of the present invention includes at least one or more suspensates because the suspensate is the active ingredient which is insoluble and suspended in the formulation and is to be deposited onto a surface and provides the auxiliary benefit. The 20 composition of the present invention is referred to as "multifunctional" because a plurality of active ingredients can be incorporated into the composition to provide several benefits to a surface. The suspensate is generally an ingredient selected to provide a certain beneficial property to the surface such as conditioning, shine, etc. The suspensate generally is a hydrophobe. The hydrophobe used in the present invention can be, but is not limited to, for 25 example a low to non-polar material that serves as an "active" (suspensate). Preferably, the hydrophobe is a dispersed oil, wax, solid or paste.

Suitable materials that can be suspended in the current composition can be described by the following formula:  $C_n H_{(2n + 2 - x)}$

where n is an integer from 6 to greater than 1 million

30 x is 0 or an even integer no greater than n.

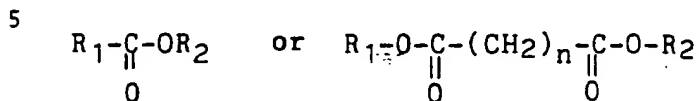
These materials include saturated, unsaturated, branched and cyclic hydrocarbon chains. Examples include: mineral oil, petrolatum, PERMETHYL™ fluids, and polybutylenes.

Other useful suspensates are the mono, di, tri or poly alkyl esters or ethers of di, tri or polyhydroxy compounds such as ethylene glycol, propylene glycol, glycerin, sorbitol or 35 polyol.

These agents include, but are not limited to the following: branched, saturated or unsaturated vegetable oils such as soybean oil, babassu oil, castor oil, cottonseed oil, Chinese tallow oil, crambe oil, perilla oil, Danish rapeseed oil, rice bran oil, palm oil, palm kernel oil,

olive oil, linseed oil, coconut oil, sunflower oil, safflower oil, peanut oil, and corn oil. Preferred saturated and unsaturated vegetable oils are those having fatty acid components with 6 to 24 carbon atoms. An example of a preferred suspensate is peanut oil.

Additional oily suspensate include esters of the type



wherein  $R_1$  and  $R_2$  are saturated or unsaturated branched or cyclic alkyl radicals of 2 to 24 carbon atoms and  $n$  is an integer from 0 to 20. Suitable esters include isopropyl palmitate and diisopropyl adipate.

The present composition may also comprise a silicone material to deliver some measure of auxiliary benefit such as lubrication or shine. The silicone material are preferably insoluble in water. Suitable water-insoluble silicone materials include polyalkylsiloxanes, polyarylsiloxanes, polyalkylarylsiloxanes, polysiloxane gums, and polyethersiloxane

15 copolymers. Teachings directed to suitable silicone materials are found in U.S. 4,788,006; U.S. 4,341,799; 4,152,416; 3,964,500; 3,208,911; 4,364,837 and U.S. 4,465,619.

Other suitable materials that can be suspended in the current composition are the type



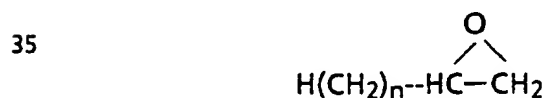
where  $R_1$  is a saturated, unsaturated, branched or cyclic alkyl radical from  $C_2$  to  $C_{24}$ ;  $M^{(+)}$  is defined by



where  $R_2$ ,  $R_3$  and  $R_4$  are hydrogen or a saturated, unsaturated or branched alkyl or hydroxyalkyl radical from  $C_1$  to  $C_{10}$ ;  $R_5$  is a saturated, unsaturated, branched or cyclic alkyl or substituted alkyl radical from  $C_2$  to  $C_{24}$ .

30 An example of the above is lauramine oleate.

Another class of suitable suspensates are formed by the polymerization of alkylene oxide monomers of the formula



where n is an integer from 0 to 3.

These materials can be either a homogeneous polymer or a copolymer of two or more monomers. Examples of homogeneous polymers include polypropylene oxide and polybutylene oxide. Typically, the molecular weights of these materials is between 100 and 10,000 daltons. Additionally, these materials can be condensed with a mono or polyhydroxyalkyl alcohol as exemplified by the UCON fluids from the Union Carbide Chemical Company.

Particulate solids can also be suspended in the current composition. A nonlimiting example includes the antidandruff agents selenium disulfide, sulfur, and compounds of pyrrithione, especially zinc pyrrithione.

The amount of suspensate used in the composition should not be so low that no deposition of the active suspensate is obtained. Too high levels of suspensate may also provide an unstable composition or suppress the foaming characteristic of the composition. A hydrophobe suspensate is inherently a foam depressor as known in the prior art. However, it is surprisingly found that in the present composition, the hydrophobe functions so as to not suppress the foam at the preferred levels of use.

Generally, the suspensate is present in the composition in an amount of from 0.001 percent to 50 percent by weight of the composition. Preferably, the hydrophobe is present in an amount of from 0.01 percent to 30 percent by weight based on the weight of the composition. More preferably, the hydrophobe is present in an amount of from 0.1 percent to 10 percent by weight based on the weight of the composition.

The composition of the present invention includes at least one or more suspending agents which serves to stabilize the suspensate in the surfactant solution. It also serves, as a secondary function, to modify viscosity of the system to improve the flow and spreading properties of the composition. The suspending agent used in the composition of the present invention can be, but is not limited to, for example, a modified polysaccharide, synthetic polymer or inorganic.

Suitable polysaccharide or polysaccharide derived suspending agents include, for example, those of cellulosic polymers, guar gums, xanthan gums, locust bean gums, gum arabic starches, starch amyloses and alginates. Excellent teachings directed to useful polysaccharides and polysaccharide derivatives are seen in The Encyclopedia of Polymer Science and Engineering, 2 ed., vol. 7, pp. 589 to 613.

Useful polysaccharide or polysaccharide derivatives are those of the guar gums and guar gum derivatives. Guar gums include those of high molecular weight carbohydrates or polysaccharides made up of linked mannose and galactose units. The molecule may be a straight chain of mannose units linked to each other by means of beta (1-4) glycosidic linkages. Galactose units may branch from alternate mannose units through alpha (1-6) linkages with the mannose units. Useful guar gums include derivatives of hydroxypropyl, hydroxyethyl,

sodium carboxymethyl, and carboxymethylhydroxypropyl guar gums. Teachings directed to guar gums are seen in U.S. Patent Nos. 4,678,606 and 4,491,539.

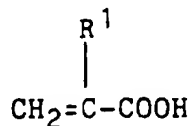
Other useful polysaccharide or polysaccharide derivatives include those of the cellulosic polymers such as methyl, ethyl, hydroxypropyl, hydroxyethyl, carboxymethyl, and  
 5 carboxymethylhydroxypropyl cellulose.

A particularly useful polysaccharide is xanthan gum. This biosynthetic gum material is commercially available and is a heteropolysaccharide with a molecular weight of greater than 1 million. It is believed to contain D-glucose, D-mannose and D-glucuronate. It is partially acetylated with approximately 5.0 percent acetyl. This information and other is found  
 10 in Whisler, Roy L., Editor, Industrial Gums - Polysaccharides and Their Derivatives, New York Academic Press, 1973.

Suitable polymeric suspending agents for the current composition are carboxyl vinyl polymers.

Carboxyvinyl polymers useful in the present invention have carboxylic acid  
 15 monomer units derived from olefinically unsaturated carboxylic acid monomers containing at least one activated carbon-to-carbon olefinic double bond, and at least one carboxyl group. The olefinic double bond readily functions in polymerization because of its presence in the monomer molecule either in the alpha-beta position with respect to a carboxyl group or as a part of a terminal methylene grouping, that is,  $\text{CH}_2<$ . Olefinically unsaturated acids in this  
 20 group include acrylic acids typified by the acrylic acid itself, methacrylic acid, ethacrylic acid, alpha-chloroacrylic acid, alpha-acrylic acid, beta methylacrylic acid (crotonic acid), alpha-phenyl acrylic acid, beta-acryloxy propionic acid, sorbic acid, alpha-chloro sorbic acid, angelic acid, cinnamic acid, p-chloro cinnamic acid, beta-styryl acrylic acid, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, maleic acid, fumaric acid, and tricarboxy  
 25 ethylene. As used herein, the term carboxylic acid includes anhydrides, as well as the polycarboxylic acids and those acid anhydrides, such as maleic anhydride, wherein the anhydride group is formed by the elimination of one molecule of water from two carboxyl groups located on the same polycarboxylic acid molecule.

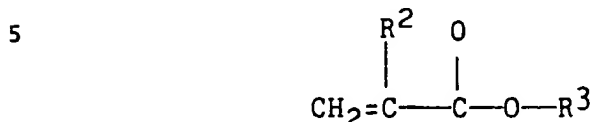
Preferred carboxylic acid monomeric units are derived from acrylic acid monomers  
 30 having the general structure



wherein  $\text{R}^1$  is a substituent selected from the class consisting of hydrogen,  
 35 halogen, and the cyanogen ( $\text{C}=\text{N}$ ) groups, monovalent alkyl radicals of 1 to 4 carbons, monovalent aryl radicals of 6 to 14 carbons, monovalent alkaryl radicals of 7 to 12 carbons, and monovalent cycloaliphatic radicals of 4 to 8 carbons atoms. Of this class, acrylic, methacrylic,

and ethacrylic acids are more preferred with acrylic acid being the most preferred. Another useful carboxylic monomer is maleic anhydride or the acid.

Suitable acrylic ester monomeric units are derived from acrylic ester monomers having the formula



where R is hydrogen, methyl or ethyl group and where R<sup>3</sup> is an alkyl group having 10 to 30 carbon atoms, preferably 12 to 22 carbon atoms. Representative acrylic esters include decyl acrylate, isodecyl acrylate, lauryl acrylate, dodecyl acrylate, stearyl acrylate, and the corresponding methacrylates. Mixtures of two or more of the long chain acrylic esters can be successfully polymerized with one or more of the carboxylic acids.

The carboxyvinyl polymers have crosslinking monomeric units derived from polyfunctional vinylidene monomers containing at least two terminal CH<sub>2</sub>-C< groups. Particularly useful crosslinking monomers are those polyalkenyl polyethers having more than one alkenyl ether group per molecule, and the most useful monomers have alkenyl groups in which an olefinic double bond is attached to a terminal methylene CH<sub>2</sub>-C<. Such monomers can be prepared by the etherification of a polyhydric alcohol containing at least four carbon atoms and at least two hydroxyl groups. Products of such reactions are complex mixtures of polyethers with varying number of ether groups. It is preferred to use polyethers containing an average of two or more alkenyl ether groups per molecule. Other crosslinking monomers can also be used. Allyl pentaerythritol, trimethylolpropane diallylether, and allyl sucrose are exceptional crosslinking monomers for purposes herein.

The carboxyvinyl polymer preferably comprises from 95 to 99, and more preferably 96 to 98 weight percent of one or more of the carboxylic acid monomeric units and preferably 5 to 1, and more preferably 4 to 2 weight percent of one or more of the acrylic ester monomeric units. The carboxyvinyl polymer further preferably comprises a small proportion of the polyethylenically unsaturated crosslinking monomeric unit. The crosslinking monomeric unit is preferably from 0.1 to 1 and more preferably from 0.1 to 0.6 weight percent of the carboxyvinyl polymer. Preferred carboxyvinyl polymers useful to the present composition are Carbopol® 1342 and 1352; Pemulen® TR1 and TR2 (all of B.F. Goodrich & Co.). Carbopol® 1342 is most preferred.

Other vinylidene monomers can be used in place of the carboxylic acid in small amounts so long as the basic properties of the carboxyvinyl polymer such as thickening or a suspending are not adversely affected. Examples include acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, styrene, vinyl toluene, vinyl methyl ether, vinyl ethyl ketone, butadiene, vinyl acetate, methyl acrylate, butyl acrylate, cyanopropyl acrylate, methoxyethyl

acrylate, chloroethyl acrylate, chloroethyl acrylate, vinyl chloride, vinylidene chloride, esters of maleic and fumaric acid, bis (8-chloroethyl) vinyl phosphonates, and the like, monomers that are known to those skilled in the art.

The carboxyvinyl polymers described herein have weight average molecular weights greater than about 500 to as high as several million. Molecular weight of such polymers is preferably in the range of 100,000 to 5 million.

Polymerization of the monomers may be carried out in the presence of a free radical catalyst in an inert atmosphere under pressure with proper agitation. Polymerization temperature may be varied from 0° to 125°C with polymerization between 25° to 90°C in presence of a free radical catalyst generally resulting in polymer yields of 75 to 100 percent. The monomers can be charged continuously or in batch during the course of polymerization or in any other conventional manner.

Useful free radical forming catalysts include, for example, peroxygen compounds such as sodium, potassium and ammonium persulfates, caprylyl peroxide, benzoyl peroxide, hydrogen peroxide, pelargonyl peroxide, cumene hydroperoxides, tertiary butyl diperphthalate, tertiary butyl perbenzoate, sodium peracetate, di(2-ethylhexyl)-peroxydicarbonate, as well as azo catalysts such as azodiisobutyryl nitrile. Other useful catalysts include the so-called "redox" type of catalyst and the heavy-metal activated catalyst systems. Ultra-violet light may also be utilized as a source of free radicals. Although some systems polymerize solely by heat, catalysts generally provide better control.

Polymerization of the monomers is conducted in a solvent or an inert organic liquid in which the monomers are soluble but the resulting polymer is insoluble. The polymerization medium can be a mixture of suitable organic liquids or solvents. The product is preferably obtained as a very fine friable or fluffy precipitate. Typical solvents include hydrocarbons containing 6 to 8 carbon atoms such as benzene, tetraline hexane, heptane, and cyclohexane; chlorinated solvents such as carbon tetrachloride, chloroform, trichloroethylene, methyl chloride ethyl chloride, and methylene chloride; chlorofluoroalkanes such as chlorofluoromethane and chlorofluoroethane containing at least 4 halogen atoms; esters such as methyl acetate and ethyl acetate; and alcohols including, for example, methanol, ethanol and butanol. Amount of organic medium used, normally will be in excess of the monomers to be polymerized and the proportion may vary from at least 1 weight percent of monomers and 99 weight percent organic medium up to about 50 weight percent monomers and 50 weight percent medium.

The carboxyvinyl polymer preferably comprises between 0.1 to 1.5, more preferably between 0.8 and 1.0, and most preferably about 0.9 weight percent of the composition.

Excellent teachings directed to carboxyvinyl polymers useful in the present composition as well as methods of making are seen in U.S. Patent No. 4,686,254.



The carboxyvinyl polymer may function as both a thickener for the composition and as a suspending agent for the oily conditioning agent. The carboxyvinyl polymer is present in an amount sufficient to suspend and stabilize the oily conditioning agent. The carboxyvinyl polymer is further preferably present in an amount and the carboxyl groups thereof are  
5 partially or substantially neutralized or esterified sufficient to thicken the composition to the desired level of thickening. The carboxyvinyl polymer is preferably 30 to 100 and more preferably 70 to 80 percent neutralized.

Suitable neutralizing agents for the carboxyvinyl polymer include those known in art as well as alkali anionic surfactants which provide the additional desired neutralizing effect.  
10 The neutralizing agent may be an organic or inorganic substance having a basic moiety capable of partially or substantially neutralizing the carboxyvinyl polymer. Useful neutralizing agents are seen in U.S. Patent Nos. 3,330,731 and 3,590,005. Useful neutralizing agents include alkali and alkaline earth metal hydroxides; mono-, di-, and tri-aliphatic amines containing from 1 to 20 carbon atoms in the aliphatic carbon chain with the same or different substituent groups in  
15 the di- and tri-compounds; and alkanolamines containing from 1 to 12 carbon atoms in the alkyl group. Suitable alkali metal hydroxides include, for example, those of sodium, potassium, and lithium. Suitable alkanolamines include mono-, di-, and tri-ethanolamines, ethanolamines, propanolamines, isopropanolamines. A most preferred neutralizing agent is triethanolamine. Also useful as neutralizing agents are the anionic acyl sarcosine surfactants described above,  
20 which neutralize the carboxyvinyl polymer in addition to providing surface activity.

Other possible suspending agents include alkali-soluble polymer emulsions such as Acrylates/Steareth-20 Methacrylate Copolymer, available as Aculyn™ 22 Thickener (Rohm and Haas Company). The use of this material is described in the Aculyn Personal Care polymers formulation bulletin, FC-116, issued in 1990, available from Rohm and Haas. Other possible  
25 suspending agents include Di(Hydrogentated) Tallow Phthalic Acid Amide, available as Stepan TAB™-2 (Stepan Company). The use of this material is described in the TAB-2 product bulletin, available from Stepan. Other possible suspending agents include liquid dispersions of sodium polyacrylate such as Sodium Polyacrylate Copolymer and Mineral Oil and PPG-1 Trideceth-6 available as Salcare SC91 (Allied Colloids). The use of this material is described in the Salcare SC-  
30 91 formulation and technical processing bulletin, available from Allied Colloids.

A suitable inorganic suspending agent can be, but is not limited to, magnesium aluminum silicate marketed as VEEGUM™ by the Vanderbilt Chemical Company.

The amount of suspending agent used in the composition should not be so low that no suspension of the suspensate is obtained. Too high levels of suspending agent would  
35 affect the processability of the composition or affect the resulting properties of the composition.

Generally, the suspending agent is present in the composition in an amount of from 0.001 percent to 10 percent by weight of the composition. Preferably, the suspending

agent is present in an amount of from 0.01 percent to 5 percent by weight based on the weight of the composition. More preferably, the suspending agent is present in a amount of from 0.1 percent to 2 percent by weight based on the weight of the composition.

The composition of the present invention includes at least one or more self-foaming or lathering-generating agents because, the self-foaming agent imparts to the composition a foam property with minimal outside mechanical energy required. The self-foaming agent can provide the ultimate composition with positive pressure for ease of dispensing or may have no positive pressure for greater versatility in choice of packaging materials. The lather-generating agent useful in the present invention can be for example a hydrocarbon or other suitable materials.

The self-foaming agent comprises at least one aliphatic hydrocarbon fluid which is a liquefiable gas or a gaseous hydrocarbon at room temperature. The gaseous hydrocarbon is preferably selected from propane, isobutane, butane, and neopentane. The self-foaming agent may further comprise at least one non-polar liquid which is substantially insoluble in water. Numerous water-insoluble non-polar liquids are described in detail in McCutcheon's "Functional Ingredients", 1991.

"Substantially insoluble" as used herein means liquids which are less than about 0.1 percent by weight soluble in water.

The water-insoluble non-polar liquid may be a substantially water insoluble nonvolatile silicone oil. The silicone oil includes polyalkylsiloxanes, polyarylsiloxanes, polyalkylarylsiloxanes, polysiloxane gums, dihydroxypolysiloxane, and polyethersiloxane copolymers.

The water-insoluble non-polar liquid is preferably an aliphatic hydrocarbon which exists as a liquid at room temperature, or is a liquid hydrocarbon. Illustrative but not limiting of the liquid hydrocarbons include: isopentane, pentane, n-hexane, isohexane, 2, 3-dimethylbutane, and mineral oil.

The vapor pressure of the aliphatic hydrocarbon fluids is primarily responsible for the vapor pressure of the composition. It has been found that higher the vapor pressure of the composition, the more rapidly the lather develops, but the composition may also be dispensed as a foam. It is useful for the purposes of this invention that the composition be substantially free from foaming, and is a liquid before and at the time of dispensation. The hydrocarbons may be so selected as to provide a composition exerting a positive pressure at least at about 1.6°C. It is preferred that the compositions exert a positive pressure at least at about 13°C (55°F). Most preferred compositions are those that exert a positive pressure at least at about 22°C. The choice of suitable hydrocarbons, alone or in combination; the concentration of hydrocarbons in the composition; and the relative ratios of component hydrocarbons if more than one hydrocarbon is used, are therefore, very critical to obtain the composition of the invention.

The weight ratio of the gaseous hydrocarbon to water-insoluble liquid generally varies in range from 5:95 to 50:50. Preferably the weight ratio of the gaseous hydrocarbon to water-insoluble liquid varies in range from 10:90 to 20:80. The self-foaming agent typically comprises from 1 percent to 20 percent by weight of the composition.

5            Preferably, the self-foaming agent is a single gaseous hydrocarbon, which is neopentane. It is suitably present in an amount from 1 percent to 5 percent by weight, based on the weight of the composition.

            More preferably, the self-foaming agent is a mixture of iso-butane or n-butane and a nonvolatile silicone oil. The nonvolatile silicone oil is preferably dimethicone.

10            Most preferably, the self-foaming agent is a mixture of at least one gaseous hydrocarbon selected from n-butane and iso-butane and at least one liquid hydrocarbon selected from iso-pentane, n-pentane, 2,3-dimethylbutane, n-hexane, isohexane, and mineral oil. The weight ratio of the gaseous hydrocarbon to liquid hydrocarbon typically varies in range from 0.5:99.5 to 99.5:0.5. Preferably the weight ratio of the gaseous hydrocarbon to  
15 liquid hydrocarbon is in the range from 10:90 to 20:80. The most preferred ratio is 20:80.

            The self-foaming agent can also be a volatile organic liquid of such a nature and in such amount that, although in liquid form at ambient temperature and having a vapor pressure substantially below atmospheric pressure, its volatilization is capable of being promoted by the combination of the aqueous soap solution and the surface active agent to an  
20 extent that a lather is generated in a practical period of time.

            The volatile organic liquid is a water-insoluble organic liquid boiling in the range from 25°C to 70°C, but preferably in the range from 35°C to 50°C. Those liquids include saturated aliphatic hydrocarbons having 5 or 6 carbon atoms, such as n-pentane, iso-pentane, n-hexane, iso-hexane, 2,2-dimethyl-butane, 2,3-dimethyl-butane, and 3-methyl-pentane, and  
25 completely halogenated hydrocarbons containing 2 carbon atoms such as 1,1,2-trichlorotrifluoroethane. Other organic liquid compounds useful here are described in U.S. Patent No. 4,744,979 incorporated herein by reference.

            The amount of self-foaming agent used in the composition should not be so low that no foaming effect is obtained yet not be so high that the composition becomes  
30 "unstable" that is, the composition should not become a multiphase system or nonhomogeneous. Also, too much of self-foaming agent can provide an unstable foam. High levels of self-foaming agent can also result in a composition that is "harsh", that is, that irritates the skin of consumer or discolors or damages a surface. If a hydrocarbon is used as a self-foaming agent, for example, too much hydrocarbon can make the composition flammable.

35            Generally, the self-foaming agent is present in the composition in an amount of from 0.01 percent to 35 percent by weight of the composition. Preferably, the lather-generating agent is present in an amount of from 0.1 percent to 20 percent by weight based on

the weight of the composition. More preferably, the self-foaming agent in the composition is from 1 percent to 10 percent by weight.

The composition of the present invention may also contain minor amounts, such as from 0 to 10 percent by weight, of one or more conventional additional ingredients to impart desired characteristics to the composition. Suitable additives include for example foam supplements, auxiliary thickening agents, humectants, coloring agents, opacifiers, perfumes, dyes, germicidal agents, preservatives, antiseptic agents, antibacterial agents, disinfectants, emollients, humectants, skin conditioners and pacifying agents.

The composition of the present invention may be prepared by simply mixing all ingredients together, and stirring them thoroughly.

In one embodiment, the present composition is prepared by using an in-line intimate mixing process using, for example, a static mixer and metering one stream of self-foaming agent into another stream comprising the remaining ingredients of the composition.

In another embodiment, the present composition is prepared by mixing all the components by shaking mechanically in well known shaking apparatus. While the ingredients of the present invention may be mixed in any suitable order, it is preferred that the self-foaming agent be contacted with the other ingredients in a final step to prevent premature foaming of the compositions. In a preferred process of making the present composition the steps include admixing the suspending agent with water, then adding the surfactant to the mixture followed by adding the hydrophobe to the mixture and then adding the self-foaming agent.

The ingredients used in the present invention can be in any useful form such as liquids, solids, pastes, flake, powder, etc. The self-foaming agent can also be introduced into the composition as a gas. The resultant composition can take the form of a liquid, gel, paste, cream or lotion.

The composition of the present invention is useful for a variety of topical applications including personal cleaning, household cleaning, industrial cleaning as well as shaving preparations. The composition of the present invention is particularly useful in a shower to be used in lieu of bar soaps and shampoos.

The composition of the present invention is also useful in many other types of cleansing applications for example shining such as wood cleaner, shoe polish, car wash and shine; deodorizing such as carpet cleaner, upholstery cleaner, pet wash; disinfecting such as toilet bowl cleaner, bathroom surface cleaner, and kitchen countertops; protecting such as upholstery, shoe/boot/leather polish, and car protectant; conditioning such as leather cleaner/conditioner; coloring such as car wash and color and shoe polish. Other applications in which the present composition can be used includes auto wash, surgical scrub, shave preparation, abrasive cleaners, oven cleaners, mildew cleaners, leather cleaner/protector, pet care and industrial cleaners.

The composition may be packaged in a pressurized or non-pressurized container depending on the nature of the ingredients used in the composition.

The following examples are illustrative of the composition of the present invention and are not intended as limitation of this invention, many apparent variations of which are possible without departing from the spirit and scope thereof. The stated amounts of the ingredients are parts by weight unless otherwise indicated.

Examples 1-47

The formulations of Examples 1-47 are described in Tables I - VIII below and were prepared as follows: Water was first added to a beaker. Carbopol (available from B. F. Goodrich) and an oil were premixed to make sure to completely disperse Carbopol. The mixture of Carbopol/oil was added to water with high shear propeller mixing and mixed until homogeneous. A surfactant was added to the water with reduced speed mixing and mixed until homogeneous. Nuocept C (available from Nuodex) was then added to the mixture. The viscosity and pH of the mixture was adjusted with TEA. The finished base was cooled to 5°C. The hydrocarbon blend was also cooled to 5°C. The specified amounts in Tables I-VIII were poured into a bottle with a leakproof closure and shaken until homogeneous.

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TABLE I - Silicone deposition  
Examples (weight percent)

<u>Ingredient</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Dimethicone	2.31	2.31	2.31	2.31	2.31	2.31
Carbopol (C10-C30 Arcylates cross polymer)	0.69	0.69	0.69	0.69	0.69	0.69
Ammonium lauryl sulfate (ALS)	20	10	8	6	4	2
Ammonium cocoyl isethionate (ACI)	15.72	7.86	6.3	4.7	3.1	1.6
Triethanolamine (TEA)	~.3	~.3	~.3	~.3	~.3	~.3
Nuoccept C (Polymethoxy Bicyclic Oxazolidine)	0.2	0.2	0.2	0.2	0.2	0.2
Water	qs 100	qs 100	qs 100	qs 100	qs 100	qs 100
BASE	96.5	96.5	96.5	96.5	96.5	96.5
80/20 isopentane/isobutane blend	3.5	3.5	3.5	3.5	3.5	3.5

TABLE II - Mineral oil deposition  
Examples (weight percent)

<u>Ingredient</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
Mineral Oil	2.31	2.31	2.31	2.31	2.31	2.31
Carbopol	0.69	0.69	0.69	0.69	0.69	0.69
ALS	20	10	8	6	4	2
ACI	15.72	7.86	6.3	4.7	3.1	1.6
TEA	~.3	~.3	~.3	~.3	~.3	~.3
Nuocept C	0.2	0.2	0.2	0.2	0.2	0.2
Water	qs 100	qs 100	qs 100	qs 100	qs 100	qs 100
BASE	96.5	96.5	96.5	96.5	96.5	96.5
80/20 isopentane/isobutane blend	3.5	3.5	3.5	3.5	3.5	3.5

TABLE III - Ester deposition  
Examples (weight percent)

<u>Ingredient</u>	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>
Propylene Glycol Isostearate	2.31	2.31	2.31	2.31	2.31	2.31
Carbopol	0.69	0.69	0.69	0.69	0.69	0.69
ALS	20	10	8	6	4	2
ACI	15.72	7.86	6.3	4.7	3.1	1.6
TEA	~.3	~.3	~.3	~.3	~.3	~.3
Nuocept C	0.2	0.2	0.2	0.2	0.2	0.2
Water	qs 100	qs 100	qs 100	qs 100	qs 100	qs 100
BASE	96.5	96.5	96.5	96.5	96.5	96.5
80/20 isopentane/isobutane blend	3.5	3.5	3.5	3.5	3.5	3.5



TABLE IV - Peanut oil deposition  
Examples (weight percent)

<u>Ingredient</u>	<u>19</u>	<u>20</u>	<u>21</u>	<u>22</u>	<u>23</u>
Peanut Oil	2.31	2.31	2.31	2.31	2.31
Carbopol 1342	0.69	0.69	0.69	0.69	0.69
Ammonium laureth sulfate	10	8	6	4	2
Ammonium cocoyl isethionate	7.86	6.3	4.7	3.1	1.6
Triethanolamine	~.3	~.3	~.3	~.3	~.3
Nuocept C	0.2	0.2	0.2	0.2	0.2
Water	qs 100	qs 100	qs 100	qs 100	qs 100
BASE	96.5	96.5	96.5	96.5	96.5
80/20 isopentane/isobutane	3.5	3.5	3.5	3.5	3.5

TABLE V - Peanut oil deposition with alt. anionic surfactant  
Examples (weight percent)

<u>Ingredient</u>	<u>24</u>	<u>25</u>	<u>26</u>	<u>27</u>	<u>28</u>	<u>29</u>
Peanut Oil	2.31	2.31	2.31	2.31	2.31	2.31
Carbopol	0.69	0.69	0.69	0.69	0.69	0.69
Sodium laureth sulfate	35.7	17.86	14.3	10.7	7.1	3.6
TEA	~.3	~.3	~.3	~.3	~.3	~.3
Nuocept C	0.2	0.2	0.2	0.2	0.2	0.2
Water	qs 100	qs 100	qs 100	qs 100	qs 100	qs 100
BASE	96.5	96.5	96.5	96.5	96.5	96.5
80/20 isopentane/isobutane blend	3.5	3.5	3.5	3.5	3.5	3.5

TABLE VI - Peanut oil deposition with alt. anionic surfactant  
Examples (weight percent)

<u>Ingredient</u>	<u>30</u>	<u>31</u>	<u>32</u>	<u>33</u>	<u>34</u>	<u>35</u>
Peanut Oil	2.31	2.31	2.31	2.31	2.31	2.31
Carbopol	0.69	0.69	0.69	0.69	0.69	0.69
Sulfoacetate/sulfosuccinate	35.7	17.86	14.3	10.7	7.1	3.6
TEA	~.3	~.3	~.3	~.3	~.3	~.3
Nuocept C	0.2	0.2	0.2	0.2	0.2	0.2
Water	qs 100	qs 100	qs 100	qs 100	qs 100	qs 100
BASE	96.5	96.5	96.5	96.5	96.5	96.5
80/20 isopentane/isobutane blend	3.5	3.5	3.5	3.5	3.5	3.5

TABLE VII - Peanut oil deposition with amphoteric surfactant  
Examples (weight percent)

<u>Ingredient</u>	<u>36</u>	<u>37</u>	<u>38</u>	<u>39</u>	<u>40</u>	<u>41</u>
Peanut Oil	2.31	2.31	2.31	2.31	2.31	2.31
Carbopol	0.69	0.69	0.69	0.69	0.69	0.69
Cl2-16 Alkoxy iminopropionate	33.33	16.67	13.33	10	6.67	3.3
TEA	~.3	~.3	~.3	~.3	~.3	~.3
Nuocept C	0.2	0.2	0.2	0.2	0.2	0.2
Water	qs 100	qs 100	qs 100	qs 100	qs 100	qs 100
BASE	96.5	96.5	96.5	96.5	96.5	96.5
80/20 isopentane/isobutane blend	3.5	3.5	3.5	3.5	3.5	3.5

TABLE VIII - Peanut oil deposition with amphoteric surfactant, and lower carb  
Examples (weight percent)

<u>Ingredient</u>	<u>42</u>	<u>43</u>	<u>44</u>	<u>45</u>	<u>46</u>	<u>47</u>
Peanut Oil	2.31	2.31	2.31	2.31	2.31	2.31
Carbopol	0.69	0.69	0.69	0.69	0.69	0.69
Cocamidopropyl Betaine	28.6	14.3	11.1	8.56	5.68	2.88
TEA	~.3	~.3	~.3	~.3	~.3	~.3
Nuoccept C	0.2	0.2	0.2	0.2	0.2	0.2
Water	qs 100	qs 100	qs 100	qs 100	qs 100	qs 100
BASE	96.5	96.5	96.5	96.5	96.5	96.5
80/20 isopentane/isobutane blend	3.5	3.5	3.5	3.5	3.5	3.5

Examples 48-59

The formulations of Examples 48-59 are described in Tables IX and X and were prepared as follows: Water was first added to a beaker. With maximum agitation, Xanthan gum, or Salcare was added to water and mixed until hydrated. Then the remaining ingredients were added. The hydrocarbon was added as in the previous Examples 1-47.

TABLE IX -Alternate thickener/suspending agent  
Examples - weight percent

<u>Ingredient</u>	<u>48</u>	<u>49</u>	<u>50</u>	<u>51</u>	<u>52</u>	<u>53</u>
Peanut Oil	2.31	2.31	2.31	2.31	2.31	2.31
Xanthan Gum	0.1	0.1	0.1	0.1	0.1	0.1
ALS	35.7	17.86	14.3	10.7	7.1	3.6
NaCl	3	3	3	3	3	3
Nuocept C	0.2	0.2	0.2	0.2	0.2	0.2
Water	qs 100	qs 100	qs 100	qs 100	qs 100	qs 100

TABLE X - Alternate thickener/suspending agent  
Examples - weight percent

<u>Ingredient</u>	<u>54</u>	<u>55</u>	<u>56</u>	<u>57</u>	<u>58</u>	<u>59</u>
Peanut Oil	2.31	2.31	2.31	2.31	2.31	2.31
Salcare SC-91	3	3	3	3	3	3
ALS	35.7	17.86	14.3	10.7	7.1	3.6
Nuocept C	0.2	0.2	0.2	0.2	0.2	0.2
Water	qs 100	qs 100	qs 100	qs 100	qs 100	qs 100

Examples 60-77

The formulations of Examples 60-77 are described in Tables XI - XIII and were prepared as described in Examples 1-47 except that the hydrocarbon blends and levels as described in Tables XI - XIII were used.

TABLE XI - Various levels and blends of post-foamer  
Examples - weight percent

	<u>Ingredient</u>	<u>60</u>	<u>61</u>	<u>62</u>	<u>63</u>	<u>64</u>	<u>65</u>
5	Example 1 material	95	96.5	98.5	95	96.5	98.5
	80/20 isopentane/ isobutane	5	3.5	1.5	0	0	0
	66/33 isopentane/ n-butane	0	0	0	5	3.5	1.5

TABLE XII - Various levels and blends of Post-foamer  
Examples - weight percent

	<u>Ingredient</u>	<u>66</u>	<u>67</u>	<u>68</u>	<u>69</u>	<u>70</u>	<u>71</u>
10	Example 1 material	95	96.5	98.5	95	96.5	98.5
15	80/20 isopentane/ isobutane	5	3.5	1.5	0	0	0
	66/33 isopentane/ n-butane	0	0	0	5	3.5	1.5

TABLE XIII - Various levels and blends of post-foamer  
Examples - weight percent

	<u>Ingredient</u>	<u>72</u>	<u>73</u>	<u>74</u>	<u>75</u>	<u>76</u>	<u>77</u>
20	Example 7 material	95	96.5	98.5	95	96.5	98.5
	80/20 isopentane/ isobutane	5	3.5	1.5	0	0	0
25	66/33 isopentane/ n-butane	0	0	0	5	3.5	1.5

#### Example 78

30 The deposition of the active of some of the above Examples of the present application was determined according to the following procedures A and B:

35

#### A. Wool Swatch Preparation and Treatment

The substrate used for the determination of the deposition of emollients was 100% worsted flannel (Style 526, Testfabrics, Middlesex, NJ). Worsteds flannel, or wool, was chosen, because it has a keratin structure and exhibits similar affinity for emollients as human skin.

- 5 Approximately 2 x 2 inch wool swatches were saturated with water. The wet swatches were centered in a custom sample holder. The sample holder suspended the swatch such that only a defined area (9.6 cm<sup>2</sup>) was treated. Approximately 0.25 g of the cleanser was applied to the swatch and rubbed with an angled end Teflon spatula for 30 seconds. The sample was allowed to rest for 30 seconds, then removed from the sample holder and rinsed with water
- 10 (temperature: 35.5 ± 0.5°C, flow rate: 6 L min<sup>-1</sup>) for 30 seconds. The swatch was finally suspended and dried overnight.

#### B. Hexane Extraction of Treated Swatch

- The treated wool swatch was centered, treated side down, over the opening of a 30 mL jar. With the rounded end of a spatula, the swatch was pushed into the jar. To the jar was added
- 15 15 mL of hexane. The jar was capped tightly and placed on a Gyrotory shaker for 5 minutes at 350 rpm. After shaking, 5 mL of the extract was removed and transferred to a sample vial. Exactly 5 mL of fresh hexane was added to the jar that contained the swatch and the sample was shaken for an additional five minutes. Again, 5 mL of extract was removed and combined with the previous 5 mL of extract in the sample vial. The procedure was again repeated, such
- 20 that a total of 15 mL of extract was collected. The combined extract was blown to dryness under dry nitrogen. Exactly 1 mL of hexane was added to the residuals in the vial and shaken by hand for 20 seconds. The extracts were transferred to auto sampler vials and analyzed by gas chromatography.

#### Deposition Test Results

- 25 Table XIV displays the results of deposition tests performed on various examples of the present invention. Measured in examples 19-23 and 24-29 is residual peanut oil left on wool swatches after washing them with the example compositions. Measured in examples 1-6 is residual dimethicone left on wool swatches. The results are shown in Figures 1, 2 and 3 wherein:

- 30 Figure 1 is peanut oil deposition on wool swatches after washing with examples 19-23.

Figure 2 peanut oil deposition on wool watches after washing with examples 24-29, and

- 35 Figure 3 is dimethicone deposition on wool swatches after washing with examples 1-6.



TABLE XIV - Deposition test results

	Example No.	% Active Surfactant	Peak Area (Counts per second)	
			<u>Peanut Oil</u>	<u>Silicone</u>
5	A	5	96032	
	B	4	122155	
	C	3	140591	
	D	2	193766	
	E	1	303089	
10	22	10	22648	
	23	5	41246	
	24	4	52201	
	25	3	45540	
	26	2	76396	
15	27	1	112117	
	1	10		664
	2	5		743
	3	4		783
	4	3		842
20	5	2		943
	6	1		995

25 Example 79

A method was been developed to evaluate the efficiency of surfactant based cleaners. The method can be used to compare cleansing efficiency of different surfactant levels in similar systems or to compare cleansing efficiency of competitive products.

## Method Outline:

## 30 Apparatus:

- 1) Wool watches, 3 inch x 3 inch with pinked edges to reduce fraying,
- 2) Glass jars, 26 ounce with lids,
- 3) Volumetric pipet, 20 mL,
- 4) Graduated cylinder, 50 mL,
- 35 5) Volumetric flasks, 1000 mL, 500 mL,
- 6) Analytical balance,
- 7) Stir plate and stir bars,

- 8) Mechanical horizontal motion shaker,
- 9) Beaker, 100 mL,
- 10) Drying rack (a rack from an oven is suitable),
- 11) Tweezers, general purpose,
- 5 12) Binder clips, 1 inch size,
- 13) Constant temperature forced air oven, maintained at 40°C.

Chemicals:

- 1) Hexane, reagent grade or better,
- 2) Water, deionized or better,
- 10 3) TEA lauryl sulfate (TEALS), 30 percent, available from Henkel Corporation, Hoboken, New Jersey,
- 4) Artificial sebum, available from Henkel Corporation, Hoboken, New Jersey.

Reagents:

- 1) 5 percent solution:
- 15 Weight 50 grams of artificial sebum into a 1000 mL volumetric flask. Add 500 mL hexane to dissolve. When Sebum is fully in solution, dilute to 1000 mL with hexane.

- 2) 10 percent TEA lauryl sulfate solution:

To 100 grams of TEA lauryl sulfate, add 900 grams of deionized water and stir until mixed.

Procedure:

- 20 A) Preparation of wool swatches:

Note: Prepare enough wool swatches for duplicate determinations of all samples plus two blanks for treatment with water only.

- 1) Place swatches in the 10 percent TEALS solution and gently stir for 1.5 minutes.
- 2) Remove swatches from the TEALS solution and thoroughly rinse each swatch under room  
25 temperature deionized water for one minute.
- 3) Place washed swatches on a drying rack and let sit overnight at room temperature.
- 4) Using only a tweezers to handle the swatches, carefully weigh and record the weight of each swatch. To identify the swatches, attach a tagged binder clip to each one immediately after weighing. Do not touch swatches with bare hands.
- 30 5) Remove binder clips and place individual swatches into 16 ounce jars. Label jars accordingly.
- 6) Add 50 mL of 5 percent artificial sebum solution to each glass jar and cap tightly. Place jars on mechanical shaker and gently agitate for 20 minutes.
- 7) Remove swatches from solution with the tweezers and attach corresponding binder clips.
- 8) Let soaked swatches air dry for 30 minutes to allow evaporation of hexane.
- 35 9) Remove binder clips and weigh dried swatches exhibiting the same caution as stated above. Record these weights next to the initial weights. Reattach binder clips to swatches.
- 10) Subtract the swatch initial weight from its sebum loaded weight. This is the initial sebum load.

## B) Sample treatment on wool swatches:

Note: Latex examination gloves must be worn during this section of the method to minimize contamination of skin oils to the swatches.

- 1) Fill a 1000 mL beaker with deionized water and place near sink.
- 5 2) Hold the swatch by the clip and wet it by dipping it into the deionized water in the 1000 mL beaker.
- 3) Place the prewet swatch on the balance and add 1.0 grams of product to be tested.
- 4) Place the swatch on the palm of one hand, product side up. Hold the clip under the thumb. With the other hand quickly spread the product evenly on the swatch using as little downward
- 10 pressure as possible. It is imperative that the surface of the swatch is covered with an even layer of product.
- 5) Let product remain on swatch for 30 seconds.
- 6) Rinse swatch under gentle pressure room temperature deionized water for 30 seconds.
- 7) Hang swatch in forced air oven for one hour at 40°C.

## 15 C) Blank determination:

Note: It will be necessary to run blank determinations on sebum loaded swatches. These must also be run in duplicate. Latex examination gloves must be worn during this section of the method to minimize contamination of skin oils to the swatches.

- 20 1) Prepare swatches as outlined in section A.
- 2) Fill a 1000 mL beaker with deionized water and place near sink.
- 3) Hold the swatch by the clip and wet it by dipping it into the deionized water in the 1000 mL beaker.
- 4) Remove swatch from the water and hold in the air by the clip for 30 seconds.
- 25 5) Place the swatch on the palm of one hand. Hold the clip under the thumb.
- 6) Rinse swatch under gentle pressure room temperature deionized water for 30 seconds.
- 7) Hang swatch in forced air oven for one hour at 40°C.

## D) Sebum loss determinations: Samples and blanks.

- 1) Allow swatches to cool to room temperature.
- 30 2) Remove binder clips and reweigh swatches. Record weights next to the initial and sebum loaded weights.
- 3) Subtract the treated swatch weight from the initial swatch weight. This is the sebum load after treatment.

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Calculations:

Sebum loss from treatment,

$$\% = \frac{[(\text{initial sebum load}) - (\text{sebum load after treatment})]}{\text{initial sebum load}} (100)$$

- 5                   Cleansing efficiency was measured as percent weight loss of sebum on wool swatches. Figure 4 demonstrates the cleansing efficiency of examples 7, 9, 10 as they are described in the present invention, and the comparative examples without the self-foaming agents (isopentane/isobutane) added. The graph of Figure 4 shows that as the level of surfactant decreases, the self-foaming agent increases the cleansing efficiency so that even at a
- 10 very low surfactant level (example 10, 1 percent surfactant) the cleansing efficiency is still superior to water.

#### Example 80

The foam height for some of the examples above was evaluated according to the following methods:

- 15 (1) Foam Height measurement for "5-second" foam height when using products without self-foaming agent (that is, for the examples shown in Figure 5)
- a. Weigh 100 gms soft water into a 250 mL graduated cylinder with stopper.
  - b. Weight in 10 gms of product.
  - c. Invert (shake) cylinder 10 times with moderate action.
  - 20 d. Set cylinder on bench and record level of foam in mLs after 5 seconds.
  - e. Repeat
- (2) Foam height measurement for "5-second" foam height when using products with self-foaming agent (for example, the example shown in Figure 6)
- a. Dispense 10 grams of product into 150 mL beaker that has a stir bar mixing
  - 25 at lowest speed.
  - b. Record foam height in mLs on the graduated beaker after 5 seconds.
  - c. Repeat.

Note: It is not possible to use the same test on both types of products (with and without self-foaming agent) due to the nature of the self-foaming agent.

- 30 Five second foam heights on examples 7A-12A without the self-foaming agent added is shown in Figure 5. The graph in Figure 5 shows the expected decrease in foam height as the level of surfactant in the compositions decrease.

- Five second foam heights on examples 7-12 as they are described in the present patent application is shown in Figure 6. The graph in Figure 6 shows that the foam height of
- 35 examples with decreasing levels of surfactants does not decrease because of the inclusion of the self-foaming agent.

1. A composition comprising a stable, homogeneous, self-foaming, cleansing composition comprising water;  
an effective amount of at least one suitable surfactant to provide required cleaning and foaming properties to the composition;  
5 an effective amount of at least one suitable suspensate to function as its intended use;  
an effective amount of at least one suitable suspending agent to suspend an active suspensate to be deposited on a surface to be cleaned; and  
an effective amount of at least one suitable self-foaming agent to provide self-  
10 lathering properties to the composition, whereby the amount of surfactant is minimized or reduced and whereby the amount of suspensate deposited on a surface is maximized.
2. The composition of Claim 1 wherein the suspensate is a hydrophobe.
3. The composition of Claim 1 wherein the surfactant comprises an anionic, cationic, amphoteric, zwitterionic nonionic surfactant or mixtures thereof.
- 15 4. The composition of Claim 3 wherein the anionic surfactant is selected from the group consisting of ammonium lauryl sulfate, sodium laureth-2 sulfate and ammonium cocoyl isethionate.
5. The composition of Claim 3 wherein the cationic surfactant is selected from the group consisting of isostearyl ethyl dimonium ethyl sulfate and PEG-10 stearamine.
- 20 6. The composition of Claim 3 wherein the nonionic surfactant is selected from the group consisting of lauramide DEA and cocamide MEA.
7. The composition of Claim 4 wherein the amphoteric surfactant is selected from the group consisting of lauroamphodiacetate and sodium C12-15 alkoxypropyl iminodipropionate.
- 25 8. The composition of Claim 1 wherein the suspending agent is selected from the group consisting of C10-30 acrylates cross polymer and xanthan gum.
9. The composition of Claim 1 wherein the suspensate is selected from the group consisting of peanut oil, silicone oil, and an ester.
10. The composition of Claim 1 wherein the self-foaming agent is selected from  
30 the group consisting of a hydrocarbon such as propane, isopentane, isobutane, pentane neopentane, non-polar liquids or mixtures thereof.
11. The composition of Claim 1 wherein the water is present in the composition in an amount of from 1 percent to 99 percent by weight of the composition.
12. The composition of Claim 1 wherein the surfactant is present in the  
35 composition in an amount of from 0.001 percent to 50 percent by weight of the composition.
13. The composition of Claim 1 wherein the suspending agent is present in the composition in an amount of from 0.01 percent to 10 percent by weight of the composition.

14. The composition of Claim 1 wherein the suspensate is present in the composition in an amount of from 0.001 percent to 50 percent by weight of the composition.

15. The composition of Claim 1 wherein the self-foaming agent is present in the composition in an amount of from 0.01 percent to 35 percent by weight of the composition.

5           16. A process comprising mixing the following ingredients: water; a surfactant; a compatible suspending agent; a hydrophobe; and a lather generating agent to form a stable, homogeneous, self-foaming cleansing composition.

17. The process of Claim 16 wherein the mixing is carried out by combining two streams in-line and passing the streams through a static mixer.

10           18. The process of Claim 16 wherein the mixing is carried out by shaking the ingredients with a shaking apparatus.

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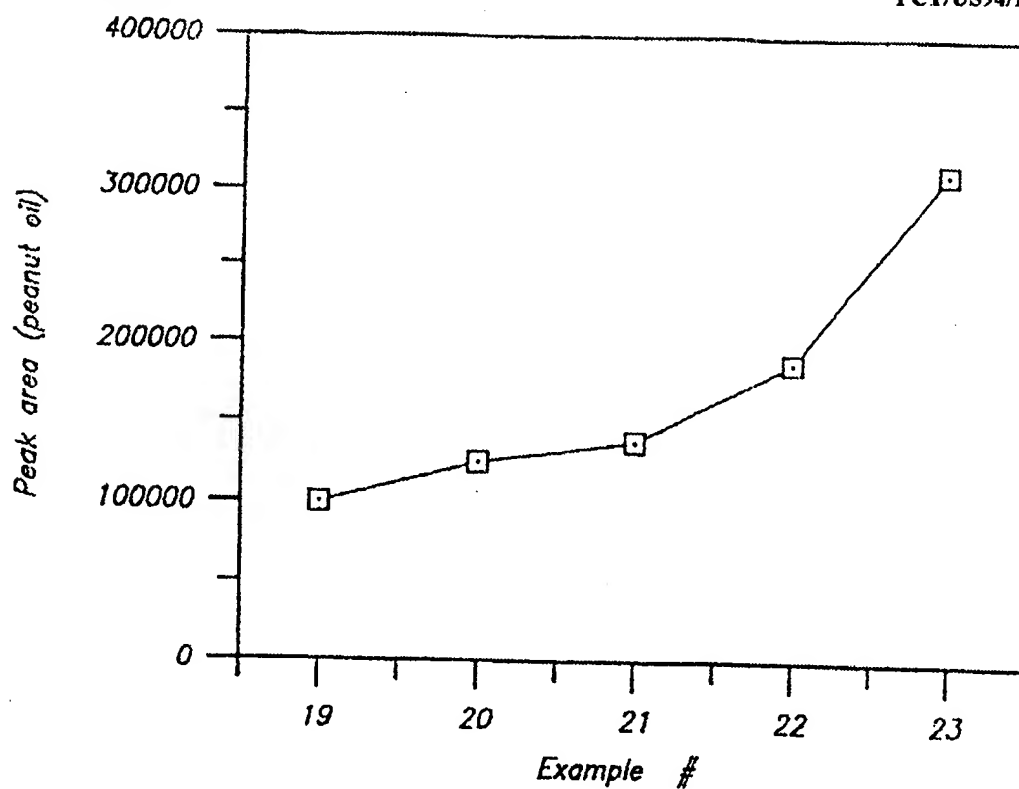


FIG. 1

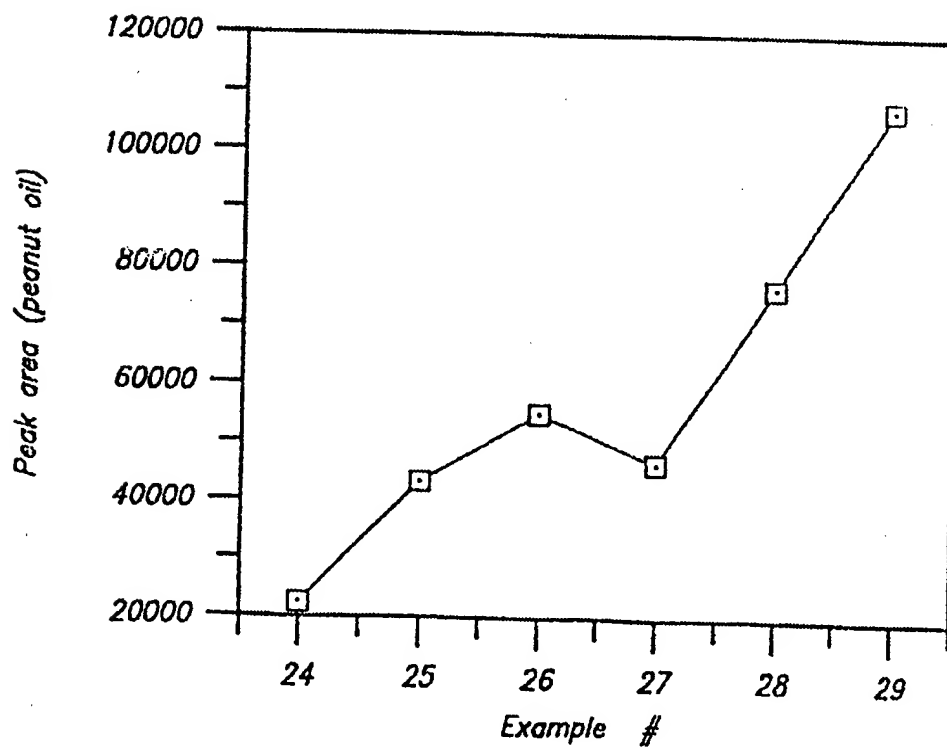


FIG. 2

1/3

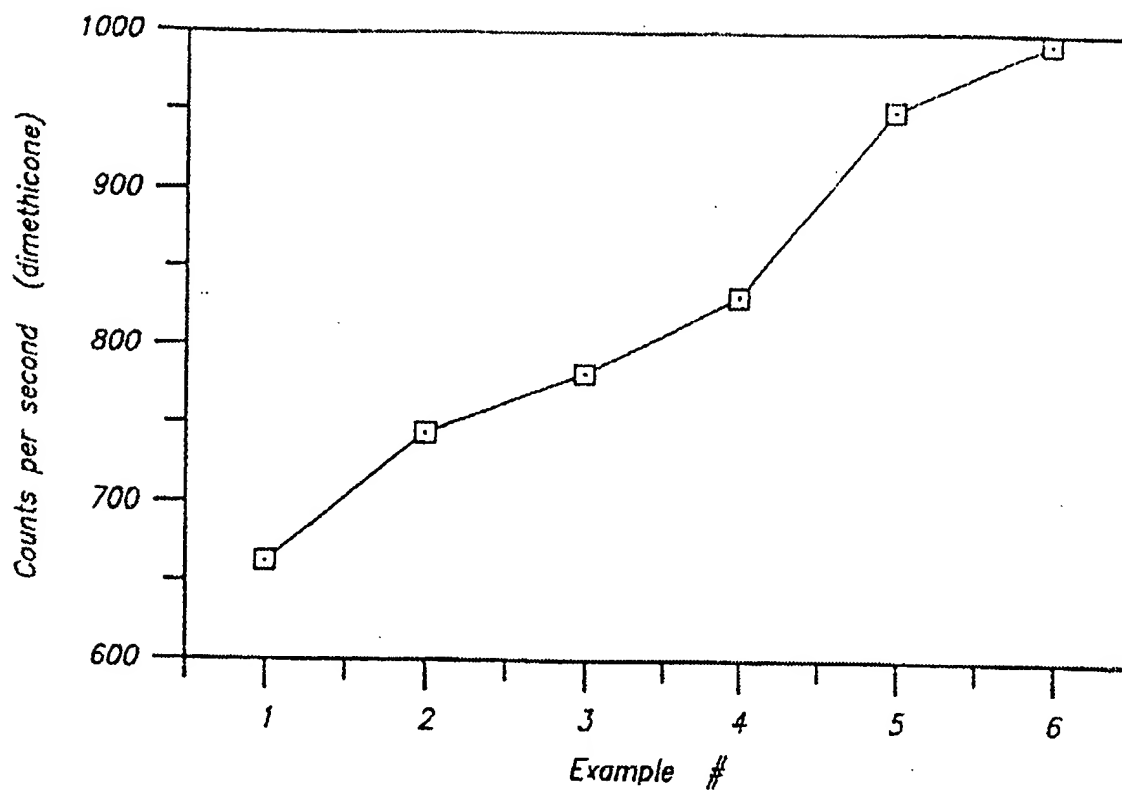


FIG. 3

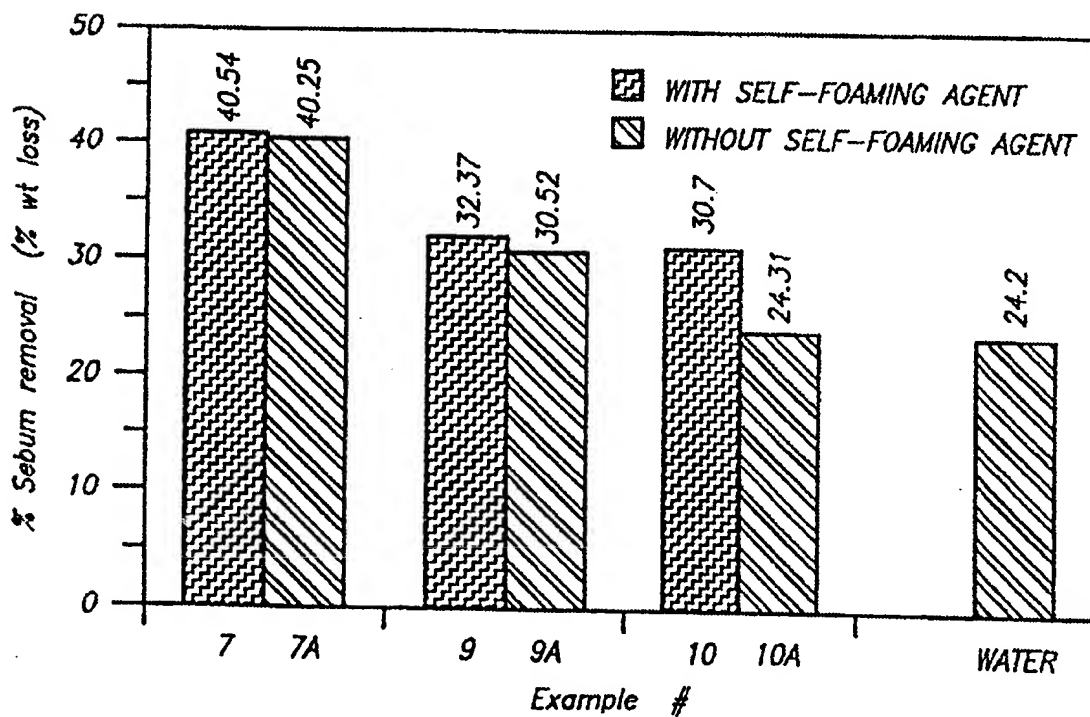


FIG. 4



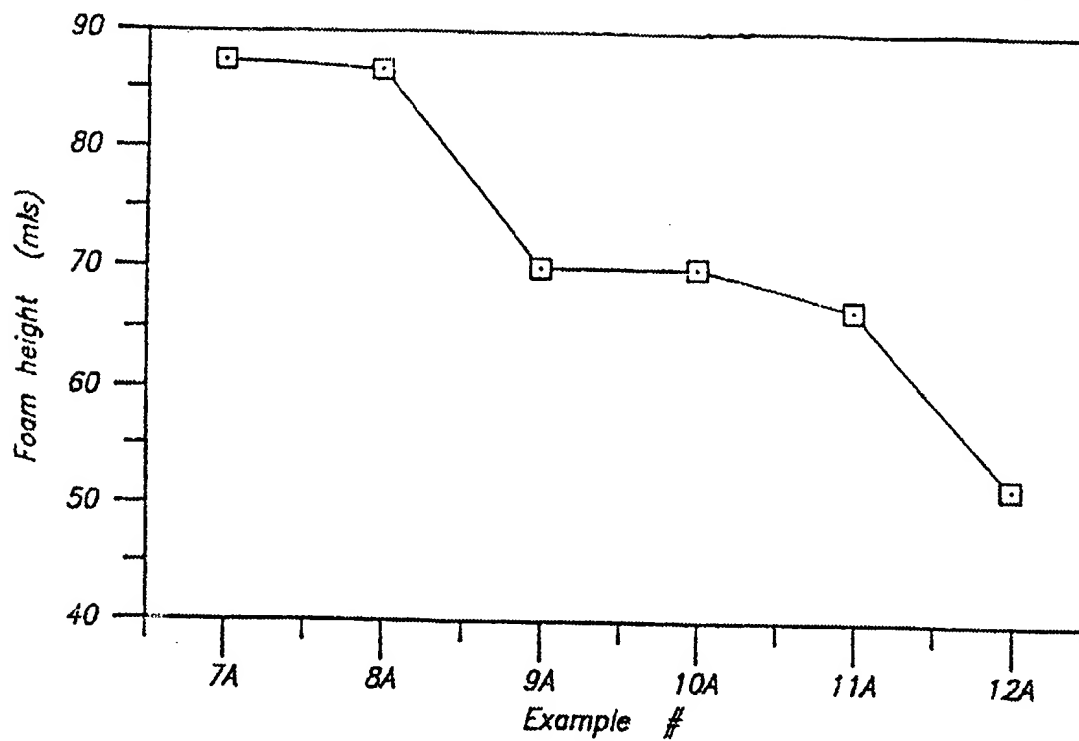


FIG. 5

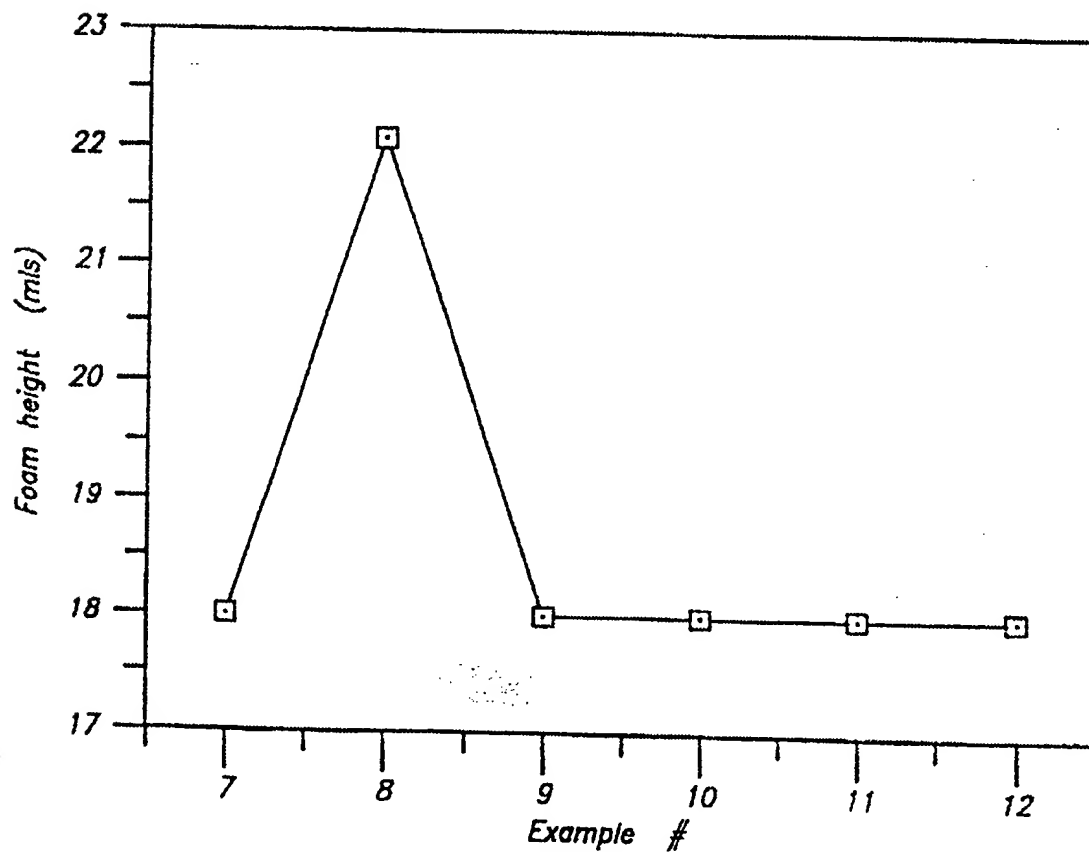


FIG. 6

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/12965

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D3/18 C11D17/00 A61K7/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,858 544 (J.ESTIGNARD-BLUARD) 20 May 1957 see example 10 ---	1-4, 10-16
X	FR,A,2 161 068 (S.C.JOHNSON) 6 July 1973 see example III ---	1-3,8-16
A	EP,A,0 247 766 (L.OSIPOW, J.SPITZER, D.MARRA) 2 December 1987 see page 4; examples ---	1
A	WO,A,90 11343 (IMAGINATIVE RESEARCH ASS) 4 October 1990 see examples ---	1,16
	--- -/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,94 02109 (DOWBRAND) 3 February 1994	1-4,8, 10-16,18
A	see page 6; claims 1-5; examples 13-16 see page 8 ---	5-7
P,X	EP,A,0 586 295 (NLN) 9 March 1994 see page 9 -----	1-3, 10-16

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 94/12965

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-858544		BE-A- 557286 DE-A, C 1419184 FR-A- 1167215 LU-A- 34385 US-A- 2995521	03-10-68 21-11-58 08-08-61
FR-A-2161068	06-07-73	US-A- 3929492 AU-B- 474867 AU-A- 4922172 CA-A- 986255 DE-A, C 2258365 DE-C- 2265378 FR-A- 1518781 GB-A- 1366593 JP-C- 1040344 JP-A- 48075487 JP-B- 55023875 NL-A- 7215873	30-12-75 05-08-76 23-05-74 30-03-76 30-05-73 26-08-82 11-09-74 31-03-81 11-10-73 25-06-80 29-05-73
EP-A-0247766	02-12-87	US-A- 4726944 DE-A- 3785484	23-02-88 27-05-93
WO-A-9011343	04-10-90	US-A- 5186857 AU-B- 628115 AU-A- 4657389 CA-A- 2001536 EP-A- 0442968 WO-A- 9005774	16-02-93 10-09-92 12-06-90 14-05-90 28-08-91 31-05-90
WO-A-9402109	03-02-94	AU-B- 4786893 CN-A- 1087380	14-02-94 01-06-94
EP-A-0586295	09-03-94	FR-A- 2695133	04-03-94